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LITHIUM FAST-ION CONDUCTORS: POLYMER BASED MATERIALS
(U) SYNTHECO INC CASTONIA NC J A WASSON 30 MAY 87

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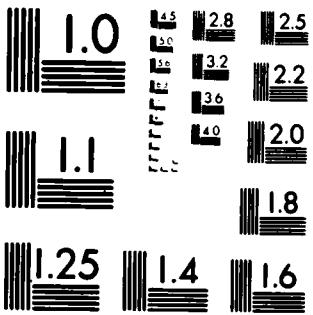
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19 ABSTRACT (Continue on reverse if necessary and identify by block number) The syntheses and room temperature conductivities of a wide variety of simple and polymeric lithium salts have been explored without finding materials with significant ambient temperature ionic conductivities. Some of the materials may be of interest in other contexts. A study of lithium tetra-fluoroborate in polyacrylonitrile showed that the composites could form the basis for a sensitive humidity sensor. Preliminary studies of a number of lithium salt-polymer systems showed that water was responsible for the observed conductivities.							
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Final Report

Lithium Fast-Ion Conductors: Polymer-Based Materials

by

John R. Wasson

SYNTHECO, Inc.

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May 30, 1987

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John R. Wasson
SYNTHECO, Inc.

Final Report

This contract, carried out by John R. Wasson as Principal Investigator, extended from July 1, 1982 to May 31, 1987 under this contract number. This work was a search for lithium-containing materials with ambient temperature ionic conductivities of 10^{-5} ($\text{ohm}\cdot\text{cm}$) $^{-1}$ or larger. The work began with an examination of simple lithium salts and was extended to lithium salt-polymer interactions. A deliberate choice was exercised in keeping these efforts out of the main stream of research involving polyether-salt complexes in order to avoid duplication of effort.

Introduction

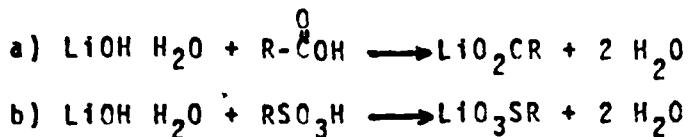
Fast-ion or superionic conductors have been the subject of extensive research efforts and potential and practical applications to batteries and other devices are known(1-8). The discovery of solids, e.g., sodium β -alumina(1), and polymer-salt complexes, e.g., $(\text{PEO})_g\text{LiClO}_4$ (3), with ionic conductivities approaching those of aqueous electrolytes, e.g., 0.1 M NaCl $\sigma=1.1 \times 10^{-2}$ ($\text{ohm}\cdot\text{cm}$) $^{-1}$, has sparked significant developments in solid state electrochemistry. Polymer-salt complexes are of particular interest because they can accommodate electrode volume changes in solid state batteries. The present work was a search for other lithium ion conducting materials with room temperature conductivities greater than 10^{-6} ($\text{ohm}\cdot\text{cm}$) $^{-1}$.

Experimental

Lithium salts were prepared by the interaction of stoichiometric quantities of lithium hydroxide monohydrate and the appropriate acid. Usually the materials were prepared on a 30-50 g scale so that samples could be provided interested parties for testing, e.g., for liquid electrolyte systems. The reactants were weighed on an analytical balance in order to keep as close as possible to the theoretical stoichiometry. The resultant salts were dried by conventional procedures, e.g., drying ovens or over desiccants. However, after extensive testing it was found best to perform final drying in a household microwave oven which had been modified with a shroud to provide a stream of dry nitrogen gas through the air intake vents (Figure 1). Samples were quickly sealed and transferred to a dry box where 13.5 mm diameter pellets were pressed and the conductivities screened using a primitive pellet technique, i.e., basically pressing a pellet between two flat copper plates and measuring the resistance with a voltmeter, cf. Ref. 9. This screening approach was standardized with a silicon reference wafer and found to be useful for conductivities greater than $10^{-7} \text{ (ohm-cm)}^{-1}$. When materials had conductivities of $10^{-6} \text{ (ohm-cm)}^{-1}$ or greater, they were sent or taken to the University of North Carolina in Chapel Hill where Professor William E. Hatfield and his group performed accurate four-point probe measurements as functions of frequency and temperature. Certain aspects of the experimental work will also be discussed in subsequent sections of this report.

Simple Lithium Salts

The initial part of the present study was an examination of simple lithium salts of carboxylic and sulfonic acids. Their preparative chemistry follows the expressions (R= organic group):



Although the chemistry is elementary, in practice the presence of impurities, e.g., H_2SO_4 in RSO_3H , and difficulties in removing traces of water complicated what should have been a straightforward study. After several months of experience it became clear that any room temperature conductivity of 10^{-6} ($\text{ohm}\cdot\text{cm})^{-1}$ was suspect and that several regrinding and redrying steps would have to be repeated. In every instance the conductivities decreased out of the range of interest.

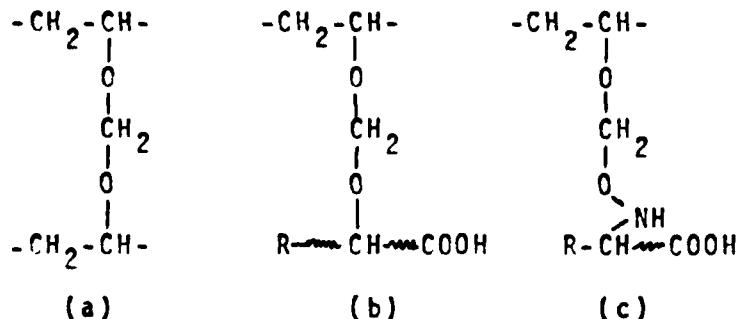
Table I summarizes most of the simple lithium salts which were examined. In passing, it is noted that lithium succinate has found use for keeping herpes infections in check(10).

Polymeric Lithium Salts

The materials employed in making polymeric lithium salts are shown in Table II. A number of polymeric anhydrides, obtained by the co-polymerization of maleic anhydride with various olefinic materials, are commonly available in good purity and offer the promise of affording good films. The anhydrides react readily with aqueous lithium hydroxide to give the lithium salts. Typically, the salts of the polymeric acids or anhydrides were prepared by dispersing the polymers in hot water, sometimes adding a little isopropanol to enhance solubility, with high speed stirring and adding a stoichiometric amount of aqueous lithium hydroxide and stirring the reaction mixture for two hours. The solutions were evaporated until gels formed and the gels were then dried in a microwave oven. The gels were ground and then redried. In most instances the materials had to be subjected to repeated grinding and drying after which the conductivities of 10^{-3} to 10^{-4} would drop to less than 10^{-6} .

$(\text{ohm cm})^{-1}$. None of the polymeric salts exhibited conductivity meeting the criterion for continued examination.

In view of work with polyethylene oxide(PEO) and polypropylene oxide systems it was decided to examine modified vinylon resins (Figure 2)(11). Vinylon resins(a) are readily prepared by reacting aqueous solutions of polyvinyl alcohol and formaldehyde. The numerous oxomethylene linkages afford ether sites similar to PEO. The vinylon resins are readily modified by incorporating hydroxy-



carboxylic (b) and aminoacids(c). The acids employed were glycine, gluconic, hydroxyacetic, lactic, malic, citric and tartaric acids and were added to the vinylon resin mixes to the extent of 5 and 10%(based on the dry weight of polyvinyl alcohol). The resultant modified vinylon resins were good cation exchange materials but the lithium salts had resistivities greater than 10^6 ohm-cm. It is noted that the vinylon resins have been developed as battery separator materials(12) and that the modified resins may have applications for membrane separations.

Other Lithium Salts

Farrington and Dunn reported(13) that lead beta"alumina has a conductivity of 4.6×10^{-3} at 40 °C. This unusual result inspired a brief study of mixed lithium-lead salts in search of a synergistic effect on conductivity. Recently, lead halide-PEO complexes have been described(R. Huq *et al.*, J. Electrochem. Soc., 134, 364(1987)). LiPbPO₄.

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$Pb_3(PO_4)_2$, Li_2PB (polyacrylate), $LiPb$ (naphthalene-1,3,6-trifulfonate) and $Pb_3(naphthalene-1,3,6-trifulfonate)_2$ were prepared and found to have room temperature conductivities of less than 10^{-6} ($\text{ohm}\cdot\text{cm}$) $^{-1}$.

Room temperature conductivity data for a number of salts are summarized in Table III.

It was of interest to prepare lithium iodide for doping into neutral polymers in later experiments. Hydriodic acid can be reacted with lithium carbonate or hydroxide and lithium iodide trihydrate obtained by evaporation of the reaction mixture. Vacuum drying of the trihydrate yields ostensibly anhydrous lithium iodide. However, detailed examination reveals the presence of about 0.1% water and other impurities among which is Li_3PO_4 , the phosphate coming from the hydriodic acid which is prepared by the hydrolysis of phosphorus iodides. An organometallic route, i.e., the reaction of n-butyl lithium with iodine in hexane(14), yields a truly anhydrous, almost white lithium iodide which contains a few(~ 50) ppm of residual hydrocarbon:

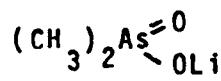
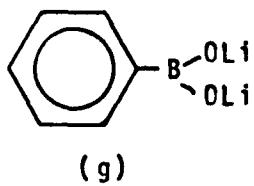
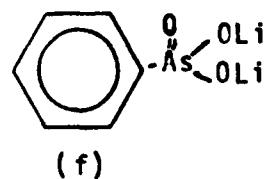
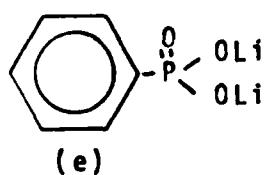
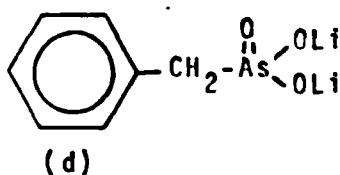


The lithium iodide is conveniently washed with dry hexane, filtered, and excess hexane removed by drying in a stream of dry nitrogen gas. The lithium iodide so prepared is very hygroscopic and seems to keep best when stored under dry hexane.

The reaction of lithium iodide in acetone with triphenylphosphine oxide results in the formation of $Li(OP\phi_3)_4I \cdot OP\phi_3$ ($\phi=C_6H_5$) in which four phosphine oxides are tetrahedrally coordinated to lithium(15). Crystals of this material were prepared and found not to meet the conductivity criterion for further study.

Lithium salts of the polyvalent anions α -toluenearsonate(d), phenylphosphonate(e), phenylarsonate(f) and phenylborate(g) as well

as the monovalent cacodylate(h) were prepared by reaction of aqueous



lithium hydroxide with the respective acids. The scrupulously dried salts all exhibited resistivities of 10^6 ohm-cm or greater. Samples of the salts were dry doped(i.e.,ground intimately and then placed in a Wig-L-Bug for 10 minutes) into PEO and supplied to Dr. John J. Fontanella at the U.S. Naval Academy for further examination.

In view of some qualitative ionic charge calculations(described later) and other considerations it was decided to prepare some materials in which lithium is bound to sulfur. Linear polyethyleneimine-lithium salt complexes have been examined by G.T. Davis and his co-workers at the National Bureau of Standards(16). Samples of non-linear aqueous polyethyleneimine, i.e., $H_2N\left(-CH_2CH_2N-\right)_xH$

where $R = \left(-CH_2CH_2NH-\right)_zH$

P-12 Avg. mol. wt.=1200, 31% NH₂, 38% NH, 31% N
 P-18 Avg. mol. wt.=1800, 29% NH₂, 38% NH, 33% N

were obtained from Cordova Chemical Co., North Muskegon, Michigan, reacted with an excess of carbon disulfide in methanol followed by reaction with methanolic lithium methoxide to yield the white solid lithium dithiocarbamate which was isolated by filtration and dried in an Abderhalden drying pistol at 55°. Attempts at microwave

drying resulted in decomposition. The samples of dried material slowly decomposed with formation of an unidentified yellow product. Attempts were made to stabilize the lithium dithiocarbamate derivative by reacting it with varying small amounts of zinc or lead salts. The mixed metal derivatives decomposed even more rapidly than the lithium compound did by itself. Conductivity work on this material was not pursued.

An alternative attempt to examine compounds with lithium bound to sulfur involved the formation of lithium thiophenolate by the reaction of n-butyl lithium in hexane with thiophenol. An off-white hygroscopic material resulted which decomposed on drying in the microwave oven. Drying required use of the Abderhalden drying pistol at 55°. Conductivities of 10^{-6} to 10^{-7} ($\text{ohm}\cdot\text{cm}$) $^{-1}$ were determined for the pure material and the material dry doped 10% by weight into PEO. Some samples exhibited conductivities of 10^{-4} ($\text{ohm}\cdot\text{cm}$) $^{-1}$ but their odors were evidence of water uptake.

Doped Polymers

Metal salt doped polymers, e.g., PEO(1-4) and poly(vinyl acetate) (17), are conveniently prepared by dissolving the metal salt and polymer in the desired ratio in a solvent and then stripping the solvent away. This approach is particularly effective for films but in bulk materials it can lead to retained solvent, i.e., a plasticized system or a solid gel electrolyte, e.g., Refs. 18 and 1-. Such plasticized systems can exhibit higher conductivities than the corresponding dry materials. Due caution has to be exercised to remove solvent in the same way one must be concerned about obtaining anhydrous materials. An alternative method, dry doping, involves grinding the polymer and salt together for extended periods and then placing the sample in a Wig-L-Bug mixer for 10 minutes. Pellets made

from LiBF₄-PEO from aqueous and dry mix routes exhibited identical conductivities. In general, though, materials obtained from solution are to be preferred.

Table IV lists polymeric materials which were investigated as host lattices for a number of lithium salts - particularly lithium hexafluoroarsenate, lithium fluoride, adipate, maleate, nitride, sulfamate, tetrafluoroborate and toluenesulfonate. Lithium trifluoromethanesulfonate and LiI(OP₃)₅ were also employed in a few instances. The object of trying several salts was to probe for anion dependence on conductivity.

In principle, lithium tetrafluoroborate is readily prepared by the reaction: LiCH H₂O + HBF₄ → LiBF₄ + 2H₂O, using aqueous tetrafluoroboric acid. Indeed that is the reaction employed in the production of lithium tetrafluoroborate. However, the hydrolysis of tetrafluoroboric acid is complex, i.e.,

$$\text{HBF}_4 + \text{H}_2\text{O} \longrightarrow \text{HBF}_3(\text{OH}), \text{HBF}_2(\text{OH})_2, \text{H}_2\text{BF}_5, \text{H}_2\text{B}_2\text{F}_6, (\text{HO})_2\text{BF}, \text{HOB(F)O(F)BOH}, \text{etc.}$$

and not all of the species and their amounts have been identified. It is known(20) that the first hydrolysis constant for HBF₄ + H₂O → HBF₃(OH) + HF has a value of K=2.3 × 10⁻³. This means that lithium tetrafluoroborate which is employed in nonaqueous battery electrolytes(21) and in other studies, e.g., LiBF₄/PEO(22), has to be considered with some caution.

In order to see if a better LiBF₄ could be obtained the reaction of n-butyl lithium in hexane with tetrafluoroboric acid etherate, i.e., N-BuLi + (C₂H₅)₂O HBF₄ → LiBF₄ + n-C₄H₁₀ + (C₂H₅)₂O was attempted in dry equipment in a nitrogen atmosphere. Only a dark brownish black oil was obtained and attempts by us and others to obtain

LiBF_4 were unsuccessful. Similar oils were obtained upon reacting anhydrous LiOH with aqueous HBF_4 in the presence of excess 2,2-dimethoxypropane and triethylorthoformate. Attempts elsewhere(23) to prepare LiBF_4 by reaction of BF_3 gas with LiF slurried in organic solvents such as diethyl ether resulted in LiBF_4 -coated LiF particles, complete conversion apparently being prevented by the lack of solubility of the LiF . It was then decided to employ LiBF_4 prepared by the aqueous route. Pellets of LiBF_4 prepared at SYNTHECO as well as of materials obtained from Foote Mineral Co. and Lithium Corporation all exhibited conductivities of 3 to 6×10^{-6} ($\text{ohm}\cdot\text{cm}$) $^{-1}$, a value in accord with that found for dry LiBF_4/PEO films(22).

The doped polymers in Table IV exhibited no room temperature conductivities of 10^{-6} ($\text{ohm}\cdot\text{cm}$) $^{-1}$ or greater over a range of concentrations of the added salt with the exception of LiBF_4 -doped PAN(polyacrylonitrile).

Polyacrylonitrile,PAN, is available from DuPont with an average molecular weight of about 150,000 in white easily powdered pellets. PAN is soluble in dimethylsulfoxide, dimethylformamide, dimethylacetamide, ethylene carbonate and other non-aqueous solvents. Heated in the absence of air PAN gives rise to semiconductive ladder polymers and ultimately graphite fibers. Films are easily cast from solution but bulk materials have to be handled carefully due to the tendency to retain solvent. Plasticized $\text{LiClO}_4/\text{PAN}$ solid electrolytes have been described(18,19). PAN can be easily dry doped from the gas phase or by mixing with molecular iodine in order to prepare cathode material for a lithium-iodine primary battery(24). PAN can also be employed in other electrical energy storage systems(25).

Watanabe et al.(18) prepared hybrid film electrolytes, i.e.,

charge, δ , acquired by an atom A can be estimated using:

$$\delta_A = S_M - S_A \gamma K(S_A)^{1/2}$$

where $K = 1.57$, S_M is the geometric mean electronegativity for the substance in which the atom is incorporated and S_A is the electronegativity for atom A. The geometric mean electronegativity for a chemical compound represented by $A_x B_y C_z$ is given by:

$$S_M = [(S_A)^x (S_B)^y (S_C)^z]^{1/(x+y+z)}$$

Sanderson's approach is simple and useful but it has its limitations. In some instances unrealistic charges for lithium and hydrogen can be calculated and the subterfuge of substituting silver must be employed. Stoklosa(35) found that Sanderson's approach was useful for economizing computer time for charge-consistent Extended-Hückel molecular orbital calculations. The lack of structure dependence on calculated results can be a severe limitation but for quick qualitative results Sanderson's method is adequate.

Table VII lists some conductivity data for lithium compounds and partial charges calculated for the lithium and silver compounds. Figure 4 shows the correlation of the calculated partial charges with the conductivities of the lithium salts. In general, the lower the charge, the greater the conductivity. Since highly polarizable ions like I^- and S^{2-} are thought to contribute to the making of good conductors(36), it was decided to qualitatively test the correlation with the work with sulfur compounds described earlier and the results were in accord with expectations based on partial charge calculations. Attempts to dry dope Li_3N into PEO were also unpromising - this, too, agrees with calculations since the amide and imide would be formed by reaction with protonic impurities.

Although Sanderson's approach has limited utility, it is useful

as a starting place for considerations of simple compounds. Better results could probably be achieved using molecular orbital calculations but at the cost of complications and increased computer time.

Summary

The purpose of this work was to make and screen lithium-containing materials in a search for ambient temperature conductivities of 10^{-5} ($\text{ohm}\cdot\text{cm}$) $^{-1}$ or larger since device grade electrolyte materials operating above room temperature are rather plentiful. Another restriction on the scope of the work was the need to focus on commercially available materials or those that could be readily made available. To this end a large number of materials were screened as opposed to detailed and extensive studies of only a few systems. The requirements for solid state electrolyte materials have been delineated in a number of places (37,38) and such factors were not ignored.

The major purpose of the work was achieved in that a large number of materials were screened. That no new good room temperature lithium ionic conductors were found is disappointing but at least a broad range of lithium materials was inspected. The work was presented and discussed in a number of meetings and seminars (listed below) and samples of several of the materials examined by other groups at Duracell, EIC, etc.

Specific conclusions based on the work are as follows:

- 1) Lithium carboxylates and sulfonates, whether simple salts or polymeric materials, are not good room temperature electrolyte materials. Doping them into PEO, PAN and other polymer hosts does not enhance their conductivities.
- 2) The single most bothersome aspect of working with lithium compounds is their extreme hygroscopicity. A microwave oven can be

modified to provide dried materials(Figure 1). Misleading conductivity results are readily encountered and special effort has to be made to obtain meaningful data.

3) The LiBF₄/PAN system provides for a rapid, reversible and sensitive(conductivity spanning eight orders of magnitude) humidity sensor material.

Presentations of Work

J.R. Wasson, D.E. Bolster and W.E. Hatfield,"Fast Ion Conductors: Lithium Ionomers and Salts - Polymer-Based Materials", The Electrochemical Society Meeting, May 8-13,1983, San Francisco.

J.R. Wasson, W.T. Ledford, D.E. Bolster and W.E. Hatfield,"Lithium Fast Ion Conductors - Polymer-Based Materials", 35th Southeastern Regional Meeting, American Chemical Society, Charlotte,N.C., Nov. 9-11,1983.

J.R. Wasson, W.T. Ledford, D.E. Bolster and W.E. Hatfield,"Lithium Fast Ion Conductors--Polymer-Based Materials", The Electrochemical Society Meeting, Cincinnati, Ohio, May 6-11,1984.

J.R. Wasson, W.T. Ledford, D.E. Bolster and W.E. Hatfield,"Fast Ion Conductors: Lithium Ionomers and Salts - Polymer-Based Materials", The Electrochemical Society Meeting, New Orleans, Oct. 7-12,1984.

J.R. Wasson, W.T. Ledford, D.E. Bolster and W.E. Hatfield,"Polymer-Based Lithium Fast Ion Conductors", 36th Southeastern Regional Meeting, American Chemical Society, Raleigh, N.C., Oct. 24-26,1984.

J.R. Wasson,W.T. Ledford and W.E. Hatfield,"Lithium Fast Ion Conductors--Polymer-Based Materials",The Electrochemical Society Meeting, Las Vegas, Oct.13-18,1985.

J.R. Wasson,"Solid State Ionic Conductors"-seminars given at:
Dept. of Chemistry, Wichita State University,Wichita,KS,Oct.1985.
Dept. of Chemistry, University of North Carolina-Chapel Hill,Aug.'86
Dept. of Chemistry, University of Southern Mississippi,Hattiesburg,
Feb. 4,1987
Carolina-Piedmont, ACS Section Meeting, Charlotte, N.C., May 26,1987
Lithium Corporation of America, Bessemer City,N.C., April 7,1987.

Follow-up Work

The work pursued in this contract will be followed up with publication of data on the LiBF₄/PAN humidity sensor system(although no device development is planned). The partial charge-conductivity correlation generality is being examined. Finally, the modified vinylon resins are being examined for their ion exchange and membrane

separation uses.

Acknowledgements

Professor W.E. Hatfield, University of North Carolina, and members of his research group performed resistivity measurement as a function of temperature and frequency on many of the samples. Dr. Hatfield's assistance and encouragement during the often frustrating efforts is appreciated. W. Troy Ledford, W. Todd Ledford and Bonnie F. Wasson assisted with some of the experimental work. The encouragement of Drs. Jerry Smith(ONR), John Bates(ORNL) and John Fontanella(U.S. Naval Academy) are appreciated.

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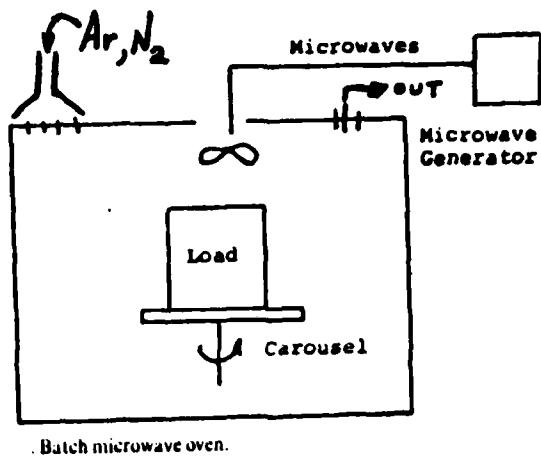
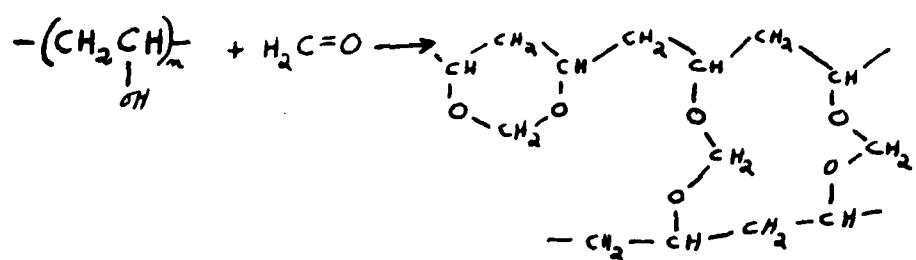


Figure 1. Modified Microwave Oven

Figure 2. Vinylon Resins



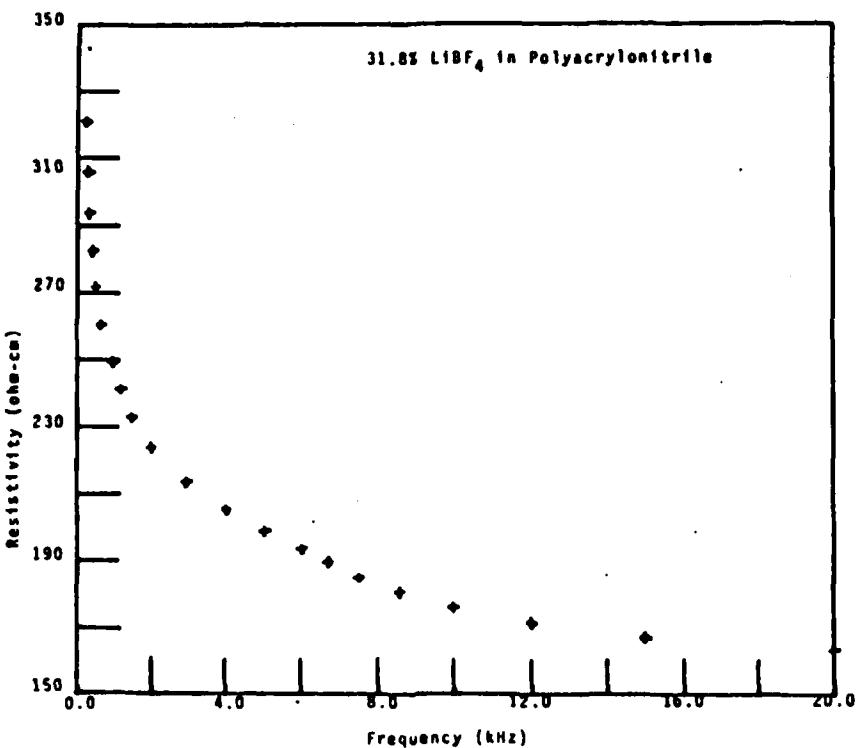
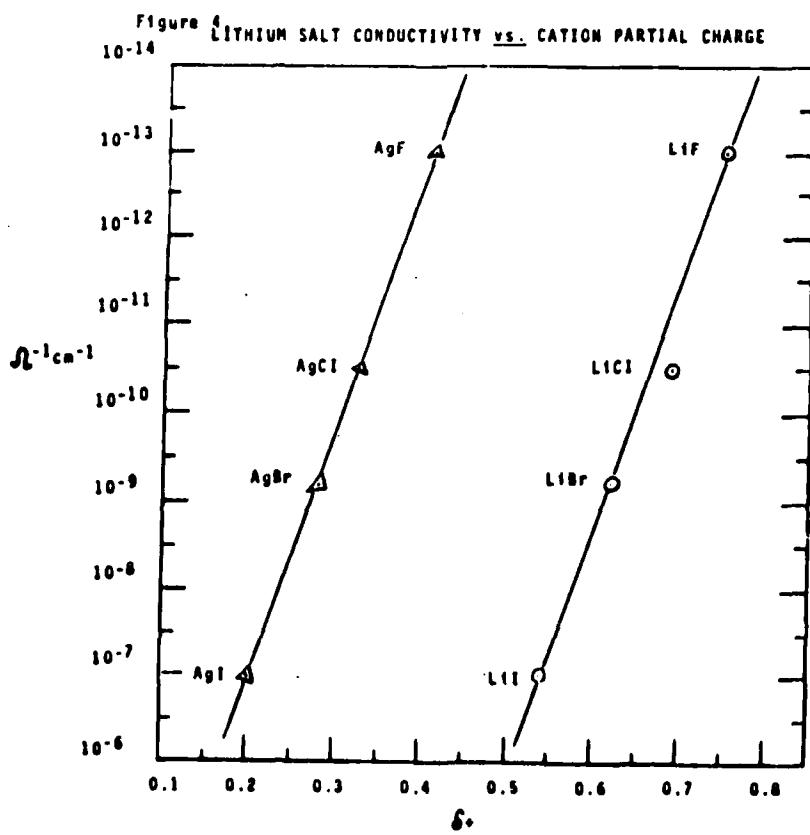
Figure 3. Typical resistivity data for the LiBF₄/PAN system.

Table I. Simple Lithium Salts Investigated.

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Acetate	Malate
Acetylenedicarboxylate	Maleate
Acrylate	Malonate
Adipate	Methanesulfonate
1-Adamantanecarboxylate	1-Naphthoate
p-Aminobenzoate	Naphthalenetrisulfonate
Behenate	Heodecanoate
Benzoate	Neopentanoate
3,3';4,4'-Benzophenonetetracarboxylate	Nicotinate
Cacodylate	Orotate
Citrate	Oxalate
3,5-Diaminobenzoate	Palmitate
1,10-Dodecanedioate	Pelargonate
2,6-Dimethoxybenzoate	Pentanoate
Dodecylbenzenesulfonate	Salicylate
Dodecylsulfate	Succinate
p-Ethylbenzenesulfonate	Sulfamate
2-Ethylhexanoate	Tartrate
Fluoroacetate	Terephthalate
Glutarate	Thiolactate
Glycinate	Thiomalate
Hydroxyacetate	p-Toluate
Indole-3-acetate	p-Toluenesulfonate
Isopentanoate	Trifluoromethanesulfonate
Laurate	
L(+) -Lactate	

Table II. Polymeric Lithium Salts Derived From:

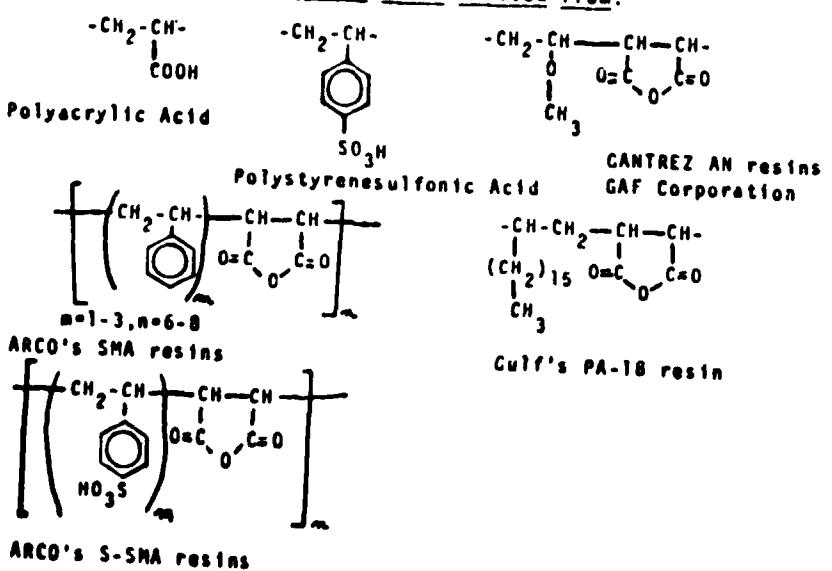
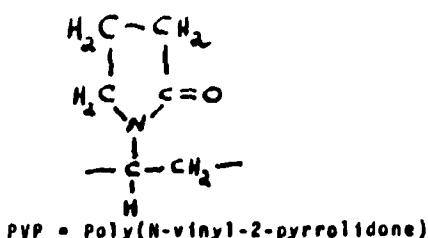
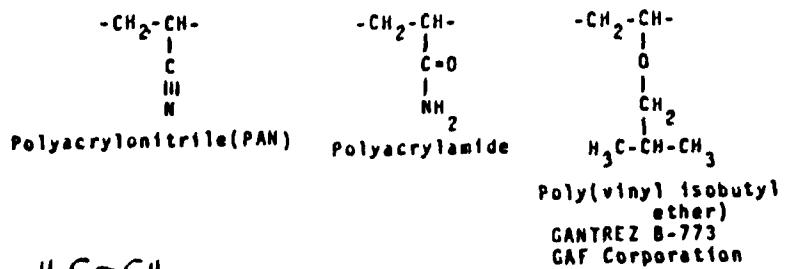


Table III. Conductivities of Lithium-Lead Salts

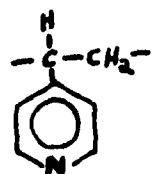
<u>Material</u>	<u>Conductivity (ohm-cm)⁻¹</u>
Li(PS)	1.18×10^{-6}
LiPb(1:3) (PS)	3.34×10^{-6}
LiPb(3:1) (PS)	8.35×10^{-7}
Li_3PO_4	5.7×10^{-8}
LiPbPO_4	6.0×10^{-8}
$\text{Pb}_3(\text{PO}_4)_2$	1.0×10^{-8}
Li_3R	$1.8-5.3 \times 10^{-7}$
LiPbR	8.3×10^{-9}
Pb_3R_2	7.1×10^{-9}

PS = polystyrenesulfonate

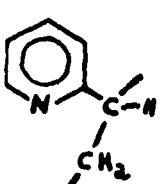
R = naphthalene-1,3,6-trisulfonate

Table IV. Polymeric Hosts for Lithium Salts

GAF Corporation
 K-30 Average molecular weight-40,000
 Soluble in water and most organic solvents



Poly(4-vinylpyridine)



Poly(2-vinylpyridine)

Table V. Plasticized Polymer Electrolytes

HYBRID FILMS Film base	$\sigma(S \cdot cm^{-1})$	Mol % Composition		
		Polymer	LiClO ₄	Plasticizer
PAN	2.0×10^{-5}	71.2	17.8	11.0(EC)
PAN	2.1×10^{-4}	50.7	12.7	36.6(EC)
PVDF	6.2×10^{-6}	56.7	24.3	19.0(EC)
PVDF	1.8×10^{-5}	39.7	17.0	43.3(EC)

PAN=poly(acrylonitrile) PVDF=poly(vinylidene fluoride)
 M. Watanabe, M. Kanba, et al., Makromol. Chem., Rapid Commun., 2, 741-744 (1981)

Table VI. Conductivity Data
LiBF₄ - Polyacrylonitrile(PAN)

Wt. % LiBF ₄	$\sigma(\text{ohm}^{-1}\text{cm}^{-1})$
6	3.09×10^{-4}
32	6.06×10^{-3}
62	1.15×10^{-4}
88	2.80×10^{-3}
95	2.95×10^{-3}

Table VII
Lithium Compounds - Conductivities and Partial Charges

Compound	$\sigma(\text{ohm} \cdot \text{cm})^{-1}$	$\delta^+(\text{Li})$	$\delta^+(\text{Ag})$
LiF	10^{-13}	0.41	0.75
LiCl	5×10^{-10}	0.33	0.67
LiBr	2×10^{-9}	0.28	0.62
LiI	1×10^{-7}	0.20	0.54
Li ₃ N	2.5×10^{-3} - 4×10^{-4}	0.25	0.13
Li ₂ NH	-----	0.56	----
LiNH ₂	-----	0.99	----
Li ₂ S	-----	0.33	----

